

II. "Compounds Isomeric with the Sulphocyanic Ethers.—III.
Transformations of Ethylic Mustard-oil and Sulphocyanide of Ethyl." By A. W. HOFMANN, Ph.D., M.D., LL.D., F.R.S.
Received November 19, 1868.

In the present paper I beg leave to communicate to the Royal Society some experiments made for the purpose of testing the views which I have lately* advanced respecting the constitution of the mustard-oils and the sulphocyanic ethers isomeric with them. These experiments were exclusively performed in the ethyl-series. Not only is ethylamine much more readily prepared than the methyl-base, but the elucidation of the metamorphoses examined was not unfrequently facilitated by the selection of compounds for the construction of which the material had simultaneously been taken from the monocarbon- and dicarbon-series.

Action of Hydrogen in condicione nascendi upon Ethylic Mustard-oil.

I have, in the first place, examined this reaction, because experiments performed by M. Oeser† have already supplied some information on the behaviour of allylic mustard-oil under analogous conditions.

On adding zinc and hydrochloric acid to an alcoholic solution of ethylic mustard-oil an evolution of sulphuretted hydrogen becomes at once perceptible; it soon diminishes, but continues for several days. In the several stages of this process the gas evolved was examined for carbonic acid; but not a trace of this gas could be detected. As soon as the evolution of sulphuretted hydrogen has ceased, the liquid is found to contain a large quantity of fine white needles; when submitted to distillation, it yields the same body, which, passing over with the vapour of water and alcohol, collects in the form of white crystals upon the water in the receiver. If the residue be now allowed to cool, an additional quantity of the crystalline compound is deposited. Analysis and examination of the properties of these crystals have identified them with the substance generated by the action of sulphuretted hydrogen upon methylaldehyde‡, to which I assigned the formula



stating at the same time that a higher molecular weight might possibly be found to belong to this sulphaaldehyde of the methyl-series.

On adding strong soda-lye to the liquid containing chloride of zinc, from which the crystals have been separated, until the oxide at first precipitated is redissolved, a strongly alkaline layer collects on the surface of the solution, which may be considerably augmented by the intervention of a small quantity of alcohol. This layer was removed and separated from adhering soda by distillation. When the very volatile distillate was saturated with

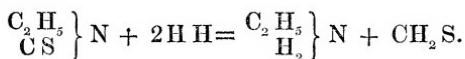
* Proceedings, vol. xvii. p. 67.

† Ann. Chem. Pharm. vol. xxxiv. p. 7.

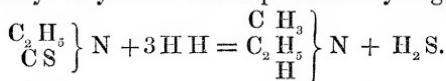
‡ Proceedings of the Royal Society, vol. xvi. p. 156.

hydrochloric acid and mixed with perchloride of platinum, the well-known hexagonal tables of the ethylamine-platinum-salt were at once deposited. The mother-liquor was found to contain a second salt, much more soluble both in water and alcohol, which was precipitated by ether. By recrystallization it was obtained in magnificent orange-red needles, which on analysis exhibited the composition of the platinum-salt of methyl-ethylamine.

The interpretation of these observations presents no difficulty. There are obviously two parallel reactions to be distinguished. In the first place (and this is doubtless the principal reaction) there are two molecules of hydrogen inserted at the place in which the two compounds of ethylic mustard-oil are joined together—this insertion giving rise to the formation, on the one hand, of ethylamine, the mother-compound of the mustard-oil, and on the other hand, of methylic sulphaldehyde, the hydrogen-derivative of bisulphide of carbon.



Or the substance, under the powerful influence of hydrogen, splits in another place; three molecules of hydrogen penetrate into the fragment of the bisulphide, and the products of this secondary and subordinate transformation are methyl-ethylamine and sulphuretted hydrogen.



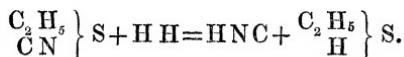
Action of Hydrogen in condicione naseendi on Sulphocyanide of Ethyl.

On treating the isomeric sulphocyanide of ethyl with zinc and hydrochloric acid, sulphuretted hydrogen is also evolved; it contains, however, so abundant an admixture of mercaptan, that the brown spot of sulphide of lead appearing upon lead-paper held over the mouth of the flask in which the reaction takes place is surrounded by a yellow ring of mercaptide of lead.

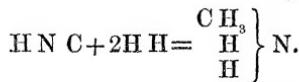
In order to examine the gases evolved, they were passed in the first place through lime-water, then through hydrate of sodium, and lastly through acetate of lead and perchloride of mercury; ultimately they were collected in a gas-holder. The lime-water remained clear; hence the gases did not contain carbonic acid; the liquid, however, was saturated with hydrocyanic acid. By the hydrate of sodium large quantities of sulphuretted hydrogen and ethyl-mercaptopan were fixed; the two metallic salts, lastly, retained some ethylic mercaptan and ethylic sulphide. The gas collected in the gas-holder was transmitted once more through lime-water and sodic hydrate, and then passed over a layer of incandescent oxide of copper. Together with water, large quantities of carbonic acid were thus produced, proving that the hydrogen contained a carbonated gas, which I do not hesitate to consider marsh-gas, although verification of this assumption, by transformation of the hydrocarbon into tetrachloride, has still to be adduced.

On distilling the liquid, when the evolution of sulphuretted hydrogen has ceased, there are evolved, together with a small quantity of the latter gas, ethylic mercaptan, sulphide and, under certain conditions, even bisulphide of ethyl, these several compounds being easily recognized by their special reactions. The residue, when heated with hydrate of sodium, disengages abundant quantities of ammonia, and also an appreciable amount of methylamine.

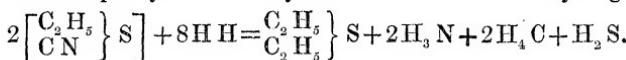
If these varied results be taken into consideration, the action of nascent hydrogen upon sulphocyanide of ethyl would appear to be a very complicated process. The principal transformation of the body is nevertheless extremely simple. Here, again, the point of junction of the two components of sulphocyanide of ethyl is the vulnerable part. A molecule of hydrogen entering at this point, between the sulphur and the carbon, the compound separates into hydrocyanic acid on the one hand and ethylic mercaptan on the other.



All the other products belong to secondary reactions. In contact with hydrogen, hydrocyanic acid is converted into methylamine.

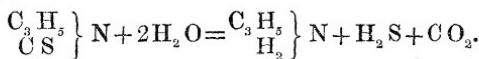


Sulphide of ethyl, ammonia, marsh-gas, and sulphuretted hydrogen may be looked upon as resulting from a further and deeper destruction of the molecule of sulphocyanide of ethyl under the influence of hydrogen.



Action of Hydrogen in condicione nascendi upon Allylic Mustard-oil.

According to the experiments of M. Oeser already quoted, the mustard-oil *par excellence*, when submitted to nascent hydrogen, would appear to undergo a transformation different from that of its ethylic congener. M. Oeser represents the metamorphosis of the allyl-compound by the following equation :—



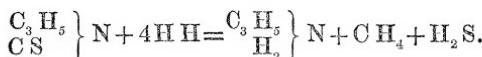
This equation, however, obviously represents no reduction process; the nascent hydrogen has no share in this reaction, which is simply accomplished under the influence of the elements of water.

To clear up this anomaly, the experiments above described were repeated in the allyl-series. On treating mustard-oil with zinc and hydrochloric acid, an abundant evolution of sulphuretted hydrogen was observed, but (under the conditions, at all events, in which I repeatedly performed this experiment) the gas did not contain a trace of carbonic acid; on the other hand, large quantities of the sulphadehyde of the methyl-series were inva-

riably obtained. If the spirit which is employed in dissolving the mustard-oil to be reduced be dilute, a fine crystallization of the sulphaldehyde is frequently observed after the lapse of a few hours. Together with this compound allylamine is generated in large proportion. The principal reaction is thus seen to be exactly the same as with ethylic mustard-oil.

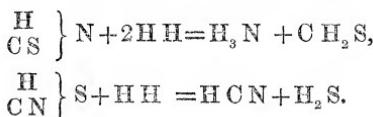


The sulphuretted hydrogen would therefore likewise belong to a secondary reaction. Vainly, however, have I endeavoured to trace in the mother-liquor of the allylamine-platinum salt the existence of the platinum compound of a second base—of methyl-allylamine for instance; though working on a rather large scale, I was unable to detect even a trace of such a compound. The origin of the sulphuretted hydrogen, however, could not be doubtful. In the gas evolved during the reaction, a large amount of a gaseous hydrocarbon (very probably marsh-gas) was present, as could be easily proved by burning the gas, after an appropriate purification, with oxide of copper.



Action of Hydrogen in condicione nascendi upon Hydrosulphocyanic Acid.

It would have been strange if in the course of these researches I had omitted to investigate the action of zinc and hydrochloric acid upon sulphocyanide of potassium. The result of this experiment could scarcely be doubtful—evolution of sulphuretted hydrogen in torrents, copious separation of sulphuretted methylic aldehyde, in the residue ammonia and methylamine. The reaction is not without interest, since the hydrosulphocyanic acid liberated by the hydrochloric acid exhibits the principal metamorphosis both of mustard-oil and the isomeric sulphocyanide of ethyl.



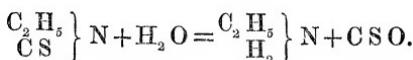
Hydrocyanic acid, it is true, is not directly observed in this case; but we meet with its hydrogen-derivative, methylamine.

Together with the behaviour of these bodies under the influence of reducing agents, I have studied the action of water and of acids upon the mustard-oils and the ethers isomeric with them.

Action of Water and Hydrochloric Acid upon Ethylic Mustard-oil.

When exposed in sealed tubes together with water to a temperature of 200° for eight or ten hours, ethylic mustard-oil splits up into ethylamine, carbonic acid, and sulphuretted hydrogen. The idea naturally suggests itself that two water-molecules act in succession. Under the influence of

the first, ethylic mustard-oil would yield ethylamine and sulphoxide of carbon.



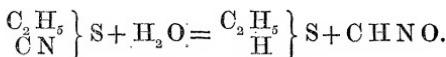
The action of the second would transform the rather unstable sulphoxide of carbon into carbonic acid and sulphuretted hydrogen.



The decomposition remains essentially the same if, instead of water, hydrochloric acid be employed. The reaction, however, is very considerably accelerated; in fact an hour's digestion at 100° is sufficient to split up the mustard-oil right off into ethylamine, carbonic acid, and sulphuretted hydrogen.

Action of Water and Hydrochloric Acid upon Sulphocyanide of Ethyl.

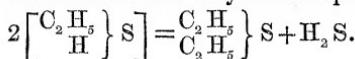
Water, even at rather high temperatures, acts but very slowly upon sulphocyanide of ethyl. Even at 200°, after several days' digestion, very appreciable quantities of the compound had remained unaltered. The reaction, as might have been expected, proceeds much more rapidly in the presence of concentrated hydrochloric acid. The ultimate products of transformation are sulphuretted hydrogen, sulphide of ethyl, carbonic acid, and ammonia. Here, again, we have by no means to deal with direct products of decomposition. Probably the compound, with the cooperation of one molecule of water, changes in the first place into ethyl-mercaptan and cyanic acid.



Under the influence of a second molecule of water, cyanic acid yields ammonia and carbonic acid.

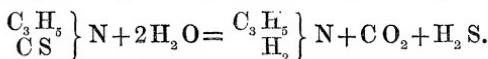


Sulphide of ethyl and sulphuretted hydrogen, lastly, have to be looked upon as products of transformation of ethylic mercaptan.



Action of Water and Hydrochloric Acid upon Allylic Mustard-oil.

Whilst engaged with these researches, I have incidentally made also some experiments upon the mustard-oil *par excellence*. As might have been expected, when submitted to the action of water at a high temperature, and more especially in the presence of hydrochloric acid, allylic mustard-oil splits up into allylamine, carbonic acid, and sulphuretted hydrogen.

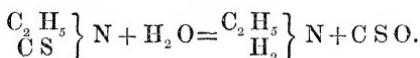


Simultaneously, however, another reaction takes place, which up to the present moment I have not yet been able to elucidate. Together with

allylamine there is formed a second liquid base having a very high boiling-point, which yields an amorphous platinum-salt. It remains behind as an oily layer, not volatilizable with the vapour of water, when the product of the action of hydrochloric acid upon mustard-oil, for the purpose of purifying the allylamine, is distilled with soda.

Action of Sulphuric Acid upon Ethylic Mustard-oil.

Dilute sulphuric acid acts like water and hydrochloric acid. Highly characteristic, however, is the behaviour of ethylic mustard-oil towards concentrated sulphuric acid. The two liquids mix with considerable evolution of heat, and after a few moments a powerful disengagement of gas takes place, which, if the reaction be promoted by the application of heat, may be increased to explosive violence. The gas evolved is inflammable, and burns with a blue flame. It has a peculiar odour, essentially different from that of bisulphide of carbon, or of sulphuretted hydrogen; from the latter it differs, moreover, by its having no action upon lead-paper. These are the characteristics of sulphoxide of carbon, lately discovered by von Than. The residue contains sulphate of ethylamine.



In contact with water, more especially in the presence of an alkali, sulphoxide of carbon is converted into carbonic acid and sulphuretted hydrogen. Treatment of ethylic mustard-oil with concentrated sulphuric acid thus enables us to arrest halfway the transformation which is accomplished under the influence of water.

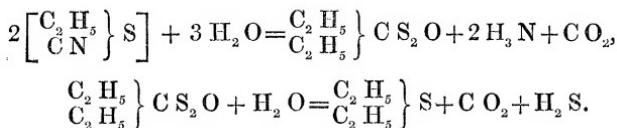
Action of Sulphuric Acid upon Sulphocyanide of Ethyl.

Dilute sulphuric acid acts but slowly upon sulphocyanide of ethyl; concentrated acid, on the other hand, attacks the compound with great energy, powerful evolution of heat and disengagement of carbonic and sulphurous acids taking place. On distilling the liquid after addition of water, sulphuretted ethereal products are volatilized; the deep-brown residue, when treated with lime, yields abundance of ammonia. In the presence of these observations, it appeared very probable that the action of sulphuric acid resembled that of water and of hydrochloric acid, and that in this case likewise the ethyl-group was eliminated in combination with sulphur.

Interesting experiments on the action of sulphuric acid upon sulphocyanide of ethyl, lately communicated to the Chemical Society of Berlin* by Messrs. Schmitt and Glutz, have indeed verified this assumption; but these experiments have proved, moreover, that the reaction, exactly as in the case of the transformation of ethylic mustard-oil, is capable of stopping at an intermediate stage, inasmuch as the above-named chemists have succeeded in isolating from the products of the reaction a compound isomeric

* Sitzungsberichte der chemischen Gesellschaft, 1868, S. 182.

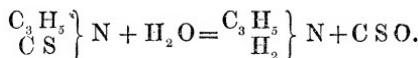
with xanthic ether. Accordingly the metamorphosis of sulphocyanide of ethyl under the influence of sulphuric acid would appear to be accomplished in the following two phases :—



It is true Messrs. Schmitt and Glutz, when submitting their ether to the action of water, obtained mercaptan, whilst, according to my observations, the products of decomposition of sulphocyanide of ethyl with hydrochloric acid are sulphide of ethyl and hydrosulphuric acid. But since two molecules of mercaptan contain the elements of one molecule of sulphide of ethyl and one molecule of sulphuretted hydrogen, the final products of decomposition of sulphocyanide of ethyl by water and by hydrochloric and sulphuric acids are virtually the same.

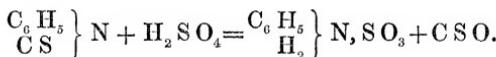
Action of Sulphuric Acid upon Allylic Mustard-oil.

Mustard-oil *par excellence*, when treated with sulphuric acid, as might have been expected, exactly imitates the behaviour of the ethyl-compound. Sulphoxide of carbon is evolved with effervescence ; the residue contains sulphate of allylamine.



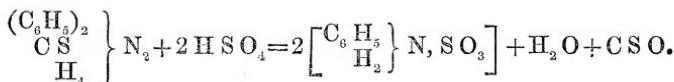
The reaction proceeds with the utmost regularity and precision. The liquid scarcely becomes coloured ; mixed with water and distilled with hydrate of sodium, it yields abundance of perfectly pure allylamine. It would be difficult to imagine a more elegant and expeditious process for preparing this interesting base in a state of perfect purity. Allylamine thus obtained was identified by the analysis of the platinum-salts, the preparation of the terribly smelling allyl-formonitril, which I shall describe in another paper, and, lastly, by its retransformation into mustard-oil, according to the method described in my last paper*.

Also phenylie and tolylie mustard-oils exhibit an analogous behaviour with sulphuric acid ; in these cases likewise sulphoxide of carbon is evolved ; the base, however, does not remain as sulphate, but in the form of an amine-sulphate in the residue.



Even phenyl-sulphocarbamide, as well as its homologues and analogues, is changed in this sense.

* Proceedings of the Royal Society, vol. xvii. p. 67.

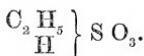


In the presence of an excess of sulphuric acid, the water-molecule eliminated is without influence upon sulphoxide of carbon.

Action of Nitric Acid upon Ethylic Mustard-oil.

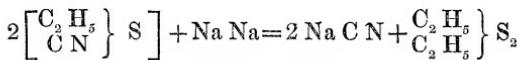
I have still to say a few words respecting the behaviour of ethylic mustard-oil with nitric acid, although the experience acquired in the several experiments I have described could not possibly leave any doubt on the nature of this reaction. Here, again, the ethyl-group separates, united with nitrogen, in the form of ethylamine, from the molecule, while the carbon and sulphur of the group CS are burnt and eliminated in the form of carbonic and sulphuric acids. The same deportment is exhibited by the homologues of ethylic mustard-oil, and also by the allyl-compound.

The products which are generated by the action of nitric acid upon sulphocyanide of ethyl and its homologues are known. According to the experiments of Muspratt, sulphocyanide of ethyl yields with nitric acid ethyl-sulphurous acid,



Accordingly there is also in this case elimination of the ethyl-group, in the form of a sulphur-compound.

In conclusion it may be stated that I have examined the action of several other chemical agents, and more especially of the alkali-metals and their hydrates, on the two classes of isomeric compounds. Most of the experiments, however, which I have made in this direction are not yet completed, and I will here only briefly allude to the elegant transformation which sulphocyanide of ethyl suffers in contact with metallic sodium. A powerful reaction ensues, cyanide of sodium and sulphide of ethyl being formed.



It affords me great pleasure to mention the energy and intelligence with which Dr. Bulk has assisted me during the performance of the experiments described in this paper. My best thanks are due to him.

III. "On the Solar Protuberances." By M. JANSSEN. In a Letter
to WARREN DE LA RUE, F.R.S. Communicated by Mr. DE LA
RUE. Received February 2, 1869.

"Je voulais vous écrire depuis longtemps pour vous faire part de mes travaux et vous remercier des bonnes et puissantes introductions que je vous dois. J'attendais que j'eusse quelque chose de complet à vous présenter, et j'ai été ainsi entraîné peu à peu."